

## PATENT ABSTRACTS OF JAPAN

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## (54) ADMIXTURE FOR CEMENT

## (57)Abstract:

**PURPOSE:** To improve slump loss preventing properties, water reducing properties and workability, comprising an esterified product of a specific copolymer and a polyoxyalkylene derivative.

**CONSTITUTION:** A polyoxyalkylene derivative of formula I (A1O is 2-4C oxyalkylene and its 50-100mol% is oxyethylene; R is 1-4C alkyl; (n) is 4-150) is copolymerized with maleic anhydride in the molar ratio of 1:0.5-1:2 in the presence of a peroxide-based polymerization initiator or an azo-based polymerization initiator, optionally with another radically polymerizable component to give (A) a copolymer, which is reacted with (B) a polyoxyalkylene derivative of formula II (R2-3 are 1-4C alkyl; A2O is 2-4C oxyalkylene; (m) is 1-300) in the ratio of the number of equivalents of acid anhydride group of maleic anhydride unit of the component A and the number of equivalents of hydroxyl group of the component B of 1:2-10:1 in the presence of an alkali, an amine, etc., as a catalyst or dehydrated in the presence of an aid catalyst or heated in the absence of the catalyst and esterified.






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CLAIMS

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[Claim(s)]

[Claim 1] (A) Component (b) general formula [1]

CH<sub>2</sub>=CHCH<sub>2</sub>O(A<sub>1</sub>O) nR<sub>1</sub> -- [1]

the polyoxyalkylene derivative shown by (however, the 50 - 100-mol % is [ the alkyl group of carbon numbers 1-4 and n of an oxyethylene radical and R<sub>1</sub> ] 4-150 in the oxy-alkylene group of carbon numbers 2-4 for A<sub>1</sub>O), and (\*\*) -- the copolymerization object which uses a maleic anhydride as an indispensable component, and (B) component general formula [2]

R<sub>2</sub>, R<sub>3</sub>, and N(A<sub>2</sub>O) mH -- [2]

It is the additive for cement which consists of an esterification reactant with the polyoxyalkylene derivative shown by (however, R<sub>2</sub> and R<sub>3</sub> are [ the oxy-alkylene group of carbon numbers 2-4 and m of the alkyl group of carbon numbers 1-4 and A<sub>2</sub>O ] 1-300).

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the additive for cement.

[0002]

[Description of the Prior Art] Conventionally, the naphthalenesulfonic acid formaldehyde condensate salt, the melamine sulfonic-acid formaldehyde condensate salt, the ligninsulfonic acid salt, etc. are used as a water reducing agent as an additive of cement compounds, such as concrete. The demand of high intensity increases to concrete and the need of lessening the amount of the water in a concrete constituent appeared in it in recent years. Although it was effective in the above-mentioned additive lessening the amount of the water in a concrete constituent, the fluid fall of the concrete constituent which happens with time, i.e., slump loss, was unavoidable. Various proposals are made in order to prevent this slump loss. Although the compound with water reducing agents, such as fine-particles-like an olefin and a maleic-anhydride copolymerization object, and a naphthalenesulfonic acid formalin condensate, is proposed by JP,60-16851,A, separation tends to occur in it and there is a trouble which becomes uneven in it. Although it is indicated by JP,59-162162,A that concomitant use with a naphthalenesulfonic acid formalin condensate salt or a melamine sulfonic-acid formalin condensate salt, and an allyl alcohol alkylene oxide addition product-partial saturation dicarboxylic acid copolymerization object is effective in prevention of slump loss, it is not necessarily enough. Although the copolymer of the polyoxyalkylene partial saturation ether and a maleic anhydride, its hydrolyzate, or the salt of that hydrolyzate is proposed by JP,63-285140,A, the field of prevention of slump loss in this case is not necessarily enough for it. Although the copolymerization object of the polyoxyalkylene partial saturation ether and a maleate is proposed by JP,2-163108,A, there is a trouble that the setting time is long in it.

[0003]

[Problem(s) to be Solved by the Invention] Prevention of the above-mentioned slump loss is the big concerns of the concrete industry, and it was anxious for quick solution. The purpose of this invention is excellent in the slump loss prevention effectiveness, and its water reducing nature is large, and is to offer the good additive for cement of workability on the occasion of use.

[0004]

[Means for Solving the Problem] In order that this invention persons may get the additive for cement which has the above-mentioned desirable property, wholeheartedly, as a result of research, they find out that the reactant of a specific copolymerization component and the nitride which has a specific oxy-alkylene group suits the purpose of this invention, and came to complete this invention based on this knowledge. That is, this invention is (A) component (b) general formula [1].

CH<sub>2</sub>=CHCH<sub>2</sub>O(A<sub>1</sub>O) nR<sub>1</sub> -- [1]

the polyoxyalkylene derivative shown by (however, the 50 - 100-mol % is [ the alkyl group of carbon numbers 1-4 and n of an oxyethylene radical and R<sub>1</sub> ] 4-150 in the oxy-alkylene group of carbon numbers 2-4 for A<sub>1</sub>O), and (\*\*) -- the copolymerization object which uses a maleic anhydride as an

indispensable component, and (B) component general formula [2]  
 R<sub>2</sub>, R<sub>3</sub>, and N(A<sub>2</sub>O) mH -- [2]

The additive for cement which consists of an esterification reactant with the polyoxyalkylene derivative shown by (however, R<sub>2</sub> and R<sub>3</sub> are [ the oxy-alkylene group of carbon numbers 2-4 and m of the alkyl group of carbon numbers 1-4 and A<sub>2</sub>O ] 1-300) is offered.

[0005] This invention is explained below at a detail. The additive for this invention cement consists of a reactant of the copolymer of the above-mentioned (A) component, and the nitride which has the oxy-alkylene group of the (B) component. As an oxy-alkylene group of the carbon numbers 2-4 shown by A<sub>1</sub>O of the general formula [1] used for the (A) component of this invention, an oxyethylene radical, an oxypropylene radical, an oxy-butylene radical, and an oxy-tetramethylen radical are raised, and the 50 - 100-mol % is an oxyethylene radical. When an oxyethylene radical is less than [ 50 mol % ], since water solubility is inadequate, high water reducing nature cannot be obtained. As an alkyl group of the carbon numbers 1-4 shown by R<sub>1</sub> of a general formula [1], a methyl group, an ethyl group, a propyl group, an isopropyl group, butyl, an isobutyl radical, and a tertiary butyl radical are raised. In the case of less than four, n of a general formula [1] will be 4-150, coagulation becomes slow, if larger than 150, viscosity will become high and manufacture will become difficult. As an alkyl group of the carbon numbers 1-4 shown by R<sub>2</sub> and R<sub>3</sub> of a general formula [2], a methyl group, an ethyl group, a propyl group, an isopropyl group, butyl, an isobutyl radical, and a tertiary butyl radical are raised. As an oxy-alkylene group of the carbon numbers 2-4 shown by A<sub>2</sub>O of a general formula [2], an oxyethylene radical, an oxypropylene radical, an oxy-butylene radical, and an oxy-tetramethylen radical are raised. The copolymerization object of the compound of a general formula [1] and a maleic anhydride can be easily obtained by carrying out copolymerization of the compound and maleic anhydride of a general formula [1] using a peroxide system polymerization initiator or an azo system polymerization initiator.

Copolymerization of the component in which other copolymerization of styrene, an alpha olefin, vinyl acetate, etc. is possible may be mixed and carried out in that case. Although the ratio of the compound of a general formula [1] and a maleic anhydride is 1:0.5-1:2 in a mole ratio, it is 1:0.9 to 1:1.2 more preferably. As for the ratio of the copolymerization object of the compound of a general formula [1], and a maleic anhydride, and the compound of a general formula [2], 1:2-10:1 are desirable at the ratio of the acid-anhydride radical number of equivalent of the maleic-anhydride unit of a copolymerization object, and the number of equivalent of the hydroxyl group of the compound of a general formula [2].

[0006] The reactant of the copolymer of the compound of a general formula [1] and maleic anhydride which are the (A) component of this invention, and the compound of the general formula [2] which is the (B) component is an esterification object, and can be easily manufactured by making alkali or amines, such as a potassium hydroxide, a sodium hydroxide, and sodium methylate, etc. react as a catalyst. Moreover, also by dehydrating using the acid catalyst of Para toluenesulfonic acid etc., it can manufacture and can manufacture also by heating with a non-catalyst further. this invention cement additive can be obtained instead of the above-mentioned manufacture approach also by one sort of a maleic anhydride and a maleic acid, or two sorts of copolymerization reactions according to the maleate and \*\* need for the compound of \*\* general formula [1], and the compound of \*\* general formula [2]. When a maleic anhydride is added, a copolymerization reaction and an ester exchange reaction occur, and the same this invention additive as said manufacture approach can be manufactured.

[0007] The amount of the additive used of this invention is 0.04 - 1 % of the weight preferably 0.02 to 2% of the weight to cement. The additive of this invention may be used together with other additives, such as a naphthalenesulfonic acid formalin condensate salt, a melamine sulfonic-acid formaldehyde condensate salt, and a polycarboxylic acid system compound, or a defoaming agent, an air entraining agent, a rusr-proofer, a setting accelerator, retarding admixture, etc. As a polycarboxylic acid system compound, there are a salt of the copolymerization object of the compound of a general formula [1] and a maleic anhydride, the copolymerization object of the methacrylic ester of the polyoxyethylene monomethyl ether and methacrylate, and the copolymerization object of styrene and a maleic anhydride, a salt of the copolymerization object of an olefin and a maleic anhydride, polyacrylate, a polymethacrylic acid salt, etc. As an additive of this invention, alkali, such as a potassium hydroxide, a

sodium hydroxide, and a calcium hydroxide, and amines may be mixed.

[0008]

[Example]

The copolymerization object of the compound of a general formula [1] and a maleic anhydride is shown in the example 1 of manufacture - the 10 1st table. It taught the 4 opening flask to which churning equipment, nitrogen entrainment tubing, a thermometer, and reflux tubing were attached by the ratio of weight % which showed the compound of a general formula [2] shown with the copolymerization object in the 2nd table in the 2nd table. Furthermore, 0.1% of the weight of the sodium methylate of a copolymerization object was added, and 100 degrees C was made to react for 3 hours. The weight average molecular weight of the obtained reactant is shown in the 2nd table.

[0009]

[Table 1]

第1表

共重合物名	一般式 [1] の化合物	(モル)	無水マレイン酸 (モル)	他の单量体 (モル)	重量平均分子量
A	CH <sub>2</sub> =CHCH <sub>2</sub> O(C <sub>2</sub> H <sub>4</sub> O) <sub>11</sub> CH <sub>3</sub>	(1.0)	1.0	—	18,000
B	CH <sub>2</sub> =CHCH <sub>2</sub> O(C <sub>2</sub> H <sub>4</sub> O) <sub>33</sub> CH <sub>3</sub>	(1.0)	1.0	—	20,000
C	CH <sub>2</sub> =CHCH <sub>2</sub> O(C <sub>2</sub> H <sub>4</sub> O) <sub>11</sub> CH <sub>3</sub>	(1.0)	1.0	—	30,000
D	CH <sub>2</sub> =CHCH <sub>2</sub> O{[(C <sub>3</sub> H <sub>6</sub> O) <sub>15</sub> (C <sub>2</sub> H <sub>4</sub> O) <sub>15</sub> ]C <sub>4</sub> H <sub>9</sub> ] <sup>12</sup> }(1.0)	1.0	1.0	—	24,000
E	CH <sub>2</sub> =CHCH <sub>2</sub> O{[(C <sub>2</sub> H <sub>4</sub> O) <sub>40</sub> (C <sub>4</sub> H <sub>6</sub> O) <sub>16</sub> ]C <sub>4</sub> H <sub>9</sub> ] <sup>122</sup> }(1.0)	1.0	1.0	—	22,000
F	CH <sub>2</sub> =CHCH <sub>2</sub> O(C <sub>3</sub> H <sub>6</sub> O) <sub>5</sub> (C <sub>2</sub> H <sub>4</sub> O) <sub>33</sub> CH <sub>3</sub>	(1.0)	1.0	—	23,000
G	CH <sub>2</sub> =CHCH <sub>2</sub> O(C <sub>2</sub> H <sub>4</sub> O) <sub>11</sub> CH <sub>3</sub>	(0.9)	1.0	スチレン(0.1)	18,000

[0010] Notes 1{ } It is shown that inside is a random-like adduct.  
 2) C4H8O shows an oxy-tetramethylen radical.

[0011]

[Table 2]

第2表

製造例	共重合物名 (重量%)	一般式 [2] の化合物	(重量%)	重量平均 分子量
1 A	(55.3)	(CH <sub>3</sub> ) <sub>2</sub> N(C <sub>2</sub> H <sub>4</sub> O) <sub>11</sub> H	(44.7)	26,000
2 B	(75.4)	(CH <sub>3</sub> ) <sub>2</sub> N(C <sub>2</sub> H <sub>4</sub> O) <sub>11</sub> H	(24.6)	27,000
3 B	(87.7)	(CH <sub>3</sub> ) <sub>2</sub> N(C <sub>2</sub> H <sub>4</sub> O) <sub>11</sub> H	(12.3)	23,000
4 B	(52.0)	(CH <sub>3</sub> ) <sub>2</sub> N(C <sub>2</sub> H <sub>4</sub> O) <sub>33</sub> H	(48.0)	28,000
5 B	(39.9)	(CH <sub>3</sub> ) <sub>2</sub> N(C <sub>2</sub> H <sub>4</sub> O) <sub>11</sub> H	(60.1)	30,000
6 C	(90.4)	(CH <sub>3</sub> ) <sub>2</sub> N(C <sub>2</sub> H <sub>4</sub> O) <sub>11</sub> H	(9.6)	30,000
7 D	(52.0)	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> N((C <sub>2</sub> H <sub>4</sub> O) <sub>15</sub> (C <sub>2</sub> H <sub>4</sub> O) <sub>15</sub> )H <sup>11</sup>	(48.0)	29,000
8 E	(49.4)	(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> N((C <sub>2</sub> H <sub>4</sub> O) <sub>40</sub> (C <sub>4</sub> H <sub>8</sub> O) <sub>10</sub> )H <sup>112</sup>	(50.6)	28,000
9 F	(51.8)	(CH <sub>3</sub> ) <sub>2</sub> N(C <sub>3</sub> H <sub>6</sub> O) <sub>5</sub> (C <sub>2</sub> H <sub>4</sub> O) <sub>30</sub> H	(48.2)	29,000
10 G	(53.5)	(CH <sub>3</sub> ) <sub>2</sub> N(C <sub>2</sub> H <sub>4</sub> O) <sub>11</sub> H	(46.5)	27,000

[0012] Notes 1{ } It is shown that inside is a random-like adduct.  
 2) C4H8O shows an oxy-butylene radical.

It mixed by the ratio of weight % which showed other additives shown with the esterification object shown in the example 11 of manufacture - the 14 2nd table in the 3rd table all over the 3rd table, and

mixture was obtained.

[0013]

[Table 3]

第3表

製造例	第2表で示した反応物 (重量%)	他の添加物 (重量%)
1 1	製造例2 (30.0)	ナフタリンスルホン酸ホルマリン 縮合物ナトリウム塩 (70.0)
1 2	製造例2 (30.0)	メラミンスルホン酸ホルマリン 縮合物ナトリウム塩 (70.0)
1 3	製造例2 (50.0)	第1表に示す共重合物A (50.0)
1 4	製造例3 (50.0)	第1表に示す共重合物B (50.0)

[0014] The trial by concrete was carried out using the reactant and mixture corresponding to the examples 1-14 of manufacture as one to example 14 example. A combination presentation and a test condition are shown below.

Combination presentation (kg/m<sup>3</sup>)

Water 166 cement 450 sand 681 crushed stones 1032 additives It is shown in the 4th table.

Water / cement ratio 36.9% fine total aggregate ratio It took out, after kneading each component of the 39.9% above for 2 minutes for a pan mixer, and the slump and the air content were measured.

Furthermore, it moved to the collapse type mixer, and mixed by per minute 2 rotation, and the slump and air content of 30 minutes, 60 minutes, and 90 minutes after were measured. Moreover, it measured also about the setting time and compressive strength, and these results were shown in the 4th table.

The same trial as examples 1-14 was performed by making into the example of a comparison the compound shown in the 1-6th examples of a comparison. The result is shown in the 4th table.

Example 1 of a comparison Example 2 of a naphthalenesulfonic acid formalin condensate sodium salt comparison Example 3 of a polyethylene-glycol monoallyl ether-maleic-acid copolymerization object sodium salt comparison Compound 75wt% of the example 1 of a comparison The example [ of a comparison / 2 / compound 25wt% of ] example 4 of a mixture comparison copolymerization of the 1st table -- a name -- example 5 of a copolymerization object comparison of the compound of a general formula [1] and maleic anhydride which were used by A copolymerization of the 1st table -- a name -- the compound of the general formula [1] used by A, and the monoester ghost by the polyoxyethylene monomethyl ether of a maleic acid -- example of copolymerization object comparison 6 Since the example 6 of a -additive-less comparison cannot knead cement mixture unless it makes [ many ] water The combination presentation was changed as follows.

Combination presentation (kg/m<sup>3</sup>)

Water 195 cement 450 sand 652 crushed stones 985 water / cement ratio 43.3% fine total aggregate ratio 40.0% [0015]

[Table 4]

第4表-1

	添加量 (対セメントwt%)	スランプ (cm)				空気量 (%)				
		混練直後	30分後	60分後	90分後	混練直後	30分後	60分後	90分後	
実 施 例	1	0.30	18.0	19.5	20.5	19.0	4.0	4.1	4.2	4.2
	2	0.28	18.0	19.0	20.0	19.0	4.1	4.1	4.2	4.1
	3	0.24	18.5	19.0	19.0	18.0	4.1	4.0	4.0	3.9
	4	0.32	17.5	18.5	20.0	19.5	4.0	4.1	4.2	4.3
	5	0.38	17.5	19.0	19.5	19.0	3.9	4.2	4.1	4.3
	6	0.30	18.0	19.0	19.5	18.5	4.0	4.0	4.0	3.8
	7	0.33	18.0	18.5	18.5	18.0	4.1	4.2	4.4	4.3
	8	0.40	18.5	19.0	18.5	17.5	4.1	4.2	4.2	4.2
	9	0.38	18.0	18.5	19.0	18.5	3.9	4.1	4.2	4.1
	10	0.30	17.5	19.0	20.0	18.5	4.0	4.1	4.1	4.2
	11	0.50	18.0	17.5	17.5	17.0	4.0	3.9	3.8	3.8
	12	0.60	18.5	17.5	17.0	16.5	4.1	4.0	4.0	3.9
	13	0.20	18.0	18.5	18.0	17.5	4.0	3.0	3.9	3.9
	14	0.22	18.0	19.0	18.5	18.0	4.0	4.1	4.0	3.9
比 較 例	1	0.75	18.0	16.0	13.5	11.5	4.0	3.8	3.7	3.6
	2	0.60	17.5	16.0	14.5	12.5	4.0	4.0	3.9	4.0
	3	0.70	18.0	16.0	13.5	12.5	4.0	4.0	3.9	3.8
	4	0.30	18.5	17.5	16.5	15.5	4.1	4.0	4.0	3.8
	5	0.50	18.5	19.0	18.5	18.0	3.9	4.0	4.1	4.1
	6	-	17.5	16.5	15.5	14.0	4.1	3.9	3.9	3.8

[0016]  
[Table 5]

第4表-2

		凝結時間(時間一分)		圧縮強度(kgf/cm <sup>2</sup> )		
		始発	終結	3日	7日	28日
実施例	1	6-30	8-10	460	625	778
	2	6-00	7-45	467	633	798
	3	5-50	7-30	471	643	801
	4	6-05	7-55	459	634	786
	5	6-00	7-50	468	635	788
	6	5-30	7-15	472	642	799
	7	7-00	8-40	456	622	766
	8	6-50	8-40	458	631	769
	9	7-10	8-55	449	618	761
	10	6-30	8-15	466	630	782
	11	6-15	8-00	449	628	774
	12	6-30	8-20	448	615	768
	13	5-30	7-10	469	632	786
	14	5-50	7-35	467	640	791
比較例	1	5-50	7-40	437	611	752
	2	9-00	10-55	429	613	755
	3	7-50	9-40	430	620	757
	4	8-20	10-00	442	630	762
	5	9-50	11-45	451	631	778
	6	5-15	7-00	312	467	605

[0017] example of comparison 1- to a slump index becoming small with time and a fluidity of 6 [ 4 and ] decreasing, a slump index does not become small with time, but, as for examples 1-14, the fluidity is held. As for the examples 2 and 5 of a comparison, the setting time is long. Moreover, since a fixed slump index cannot be obtained unless it makes [ many ] the amount of water, but the amount of water can be lessened if the additive of this invention is used compared with small compressive strength and a fixed slump index can be obtained when you have no additive, compressive strength is large.

[0018]

[Effect of the Invention] By making the reactant of the copolymer of the polyoxyalkylene derivative of copolymerization nature, and a maleic anhydride, and a specific polyoxyalkylene derivative with a nitrogen atom into an active principle, the additive of this invention is an object which has high slump loss tightness and high water reducing nature, and has the outstanding workability.

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